

This fish has a superficial resemblance to the *Lepomis mystacalis*. The ends of the long gill-rakers are obtuse, as in the *L. apiatus*. There are no palatine teeth. It resembles also in form and coloration the *Pomotis microlophus*, Gthr. (*P. speciosus*, Holbr.) from the St. John's River, Florida, a species which I have not seen. According to Dr. Holbrook's figures and descriptions, there is a material difference in the radial formula which is, D. X .10; A. III .9. The form of the dorsal fin is also very different, the second being the higher, and separated from the first by a deep notch, which leaves one spine with the soft rays.

I have this species from near Volusia, and also from near Bayport on the West Coast.

*Archirus mollis*, De Kay.

Radii, D. 48; A. 35. Length without caudal fin .078; depth of body .042.

CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.

No. X.

*Dichlorsalicylic Acid.*

BY EDGAR F. SMITH, PH. D.,

*Assistant in Analytical Chemistry, University of Pennsylvania.*

(Read before the American Philosophical Society, June 15, 1877.)

As early as 1845, Cahours (*Annalen der Chemie und Pharmacie*—52. pp. 340 and 341) described a di-chlor acid which he obtained about the same time he was investigating the di-bromine substitution products of salicylic acid.

The course he pursued to produce the compound was to treat an aqueous solution of salicylic acid with an excess of chlorine. According to his description the acid thus obtained possesses great stability and can very readily be obtained pure.

And again by allowing a slow current of chlorine gas to stream through a dilute solution of potassium salicylate potassium dichlorsalicylate was formed. This salt after repeated recrystallization was obtained in almost colorless needles.

The acid corresponding to this salt was precipitated in white masses upon the addition of dilute hydrochloric acid to a solution of the latter. The acid is soluble in boiling alcohol, from which upon cooling, it separates in needles. Well formed octahedral crystals were secured by allowing a rather dilute solution to evaporate slowly in the air. Boiling water dissolves but small quantities of this acid, which separate out again in very fine needles when the solution becomes cool. Boiling concentrated nitric acid dissolves the compound, and when the liquid cools, beautiful yellow

plates separate out. By distilling the acid with barium oxide dichlorphenol (Acide Chlorophénèsique) was produced, with liberation of carbon dioxide.

Recently, Rogers (Inaugural Dissertation, Göttingen, 1875) published the results of an investigation upon a similar acid. By conducting a calculated amount of chlorine gas into a solution of salicylic acid in glacial acetic acid, and applying heat, he produced dichlorsalicylic acid, which crystallized from the above solution in small white needles. The acid was purified by converting it into its barium salt, and this then recrystallized. The acid from the purified salt fused at  $224^{\circ}\text{C}$ . It was entirely insoluble in cold, soluble in an excess of hot water and very soluble in hot alcohol.

The following salts were made and analyzed :

*Dichlorsalicylate of Barium.*— $(\text{C}_6 \text{H}_2 \text{Cl}_2 \text{OH COO})_2 \text{Ba} + 5 \text{H}_2\text{O}$ . Long needles, colored slightly brown.

*Dichlorsalicylate of Potassium.*— $\text{C}_6 \text{H}_2 \text{Cl}_2 \text{OH. C O O K}$ . Showed a tendency to crystallize in small white needles, which lost, by exposure to the air, any water of crystallization they may have possessed.

*Dichlorsalicylate of Copper.*— $(\text{C}_6 \text{H}_2 \text{Cl}_2 \text{OH C O O})_2 \text{Cu}$ . Green, insoluble precipitate.

Some time ago I had occasion to make dichlorsalicylic acid, but as I obtained a compound not corresponding to any known analogous derivative, I submit to the Society the following results of my investigation upon the new dichlorine product.

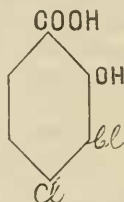
#### FORMATION OF DICHLORSALICYLIC ACID.

About 40 Grm. of pure salicylic acid (fusing point  $156^{\circ}\text{C}$ ) were placed in a flask and upon this was poured a rather large quantity of concentrated acetic acid. While applying a gentle heat to effect solution, a calculated amount of dried chlorine gas was introduced into the liquid, which gradually assumed a deep yellow color. Without waiting for the new acid to crystallize out I added to the yet warm solution a large quantity of water, whereupon the dichlorsalicylic acid fell out in large white flocks. The liquid was filtered off and the acid washed with cold water and then boiled with an excess of barium carbonate. The salt thus obtained was redissolved and recrystallized until it was obtained in almost colorless needles, which crystallize in aggregated masses from an aqueous solution. Upon several occasions monochlorsalicylate of barium was produced, but as this salt is much more soluble than the corresponding compound of the dichlor acid it was easily removed.

*Properties*—The dichlor acid separates in large flocculent masses upon the addition of dilute hydrochloric acid to a solution of the barium salt. Cold water does not dissolve the acid, an excess of boiling water being necessary to effect its solution. After many recrystallizations the acid fused at  $212^{\circ}$ – $214^{\circ}\text{C}$ . It separates from an aqueous solution in white arborescent masses. In cold alcohol it is very soluble. By the slow evaporation of such a solution stellated masses consisting of large colorless needles were obtained. The fusing point of these was the same as that of the white

crystals. The acid is sublimable with partial decomposition. A drop of ferric chloride added to its aqueous solution imparts to the latter a beautiful violet coloration.

The acid is very probably Parachlormetachlor-ortho-oxyhenzoic acid and may be graphically represented as follows :



A combustion was made of the barium salt.

*Carbon and Hydrogen Determination.* 0.2092 Grm. barium salt dried at 180° C for several hours were burned with coarse and fine lead chromate, and gave 0.241 Grm. CO<sub>2</sub>=0.065 Grm. carbon = 30.9% C. Farther .012 Grm. H<sub>2</sub>O=0.57% H.

#### SALTS.

DICHLORSALICYLATE OF BARIUM.



This salt was produced by boiling the free acid with an excess of barium carbonate. Boiling water dissolves it very readily. In cold water it is insoluble. From an aqueous solution it crystallizes in large, almost colorless needles, which are usually combined to aggregated masses.

#### *Water Estimation.*

0.6026 Grm. air-dried salt lost upon being heated for three hours at 180° C .0623 Grm. H<sub>2</sub>O=10.34% H<sub>2</sub>O.

The calculated percentage of water for 3½ molecules equals 10.29%.

Calculated.	Found.
(C <sub>6</sub> H <sub>2</sub> Cl <sub>2</sub> OH COO) <sub>2</sub> Ba=551=89.71%.	
+ 3½ H <sub>2</sub> O = 63=10.29%.	10.34
<hr style="width: 50%; margin-left: auto; margin-right: 0;"/> 614=100.00%.	

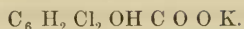
#### *Barium Estimation.*

I. 0.5403 Grm. anhydrous salt were placed in a platinum crucible, a few drops of sulphuric acid then added, and this then evaporated to dryness. 0.2227 Grm. barium sulphate were obtained, corresponding to 0.1309 Grm. barium=24.16% Ba.

II. 0.6075 Grm. anhydrous salt gave 0.2550 Grm. barium sulphate, equaling 0.1499 Grm. barium=24.67% Ba.

Calculated %.	Found %.
Cl <sub>14</sub> =168=30.60	30.90
H <sub>6</sub> = 6= 1.09	.57
O <sub>6</sub> = 96=18.60	
Cl <sub>4</sub> =142=25.86	
Ba=137=24.95	24.16 and 24.67

## DICHLORSALICYLATE OF POTASSIUM.



This salt was obtained by boiling the preceding compound with a calculated amount of potassium carbonate. From a concentrated aqueous solution it crystallized in white needles, very much like the salt of Rogers described above. After recrystallizing the compound several times and then allowing it to separate from a dilute solution I obtained it in almost colorless needles, that united to form clusters.

Analysis proved it to be anhydrous.

*Potassium Estimation.*

I. 0.2020 Grm. well dried salt gave 0.0710 Grm. potassium sulphate=.03181 K=15.75% K.

II. .2651 Grm. dried salt gave .0930 Grm. potassium sulphate=.04117 Grm. K=15.5% K.

Calculated %.	Found %
$C_6 H_2 Cl_2 OH COO=206=84.05\%$	
+ K = 39.1=15.95%	15.75% and 15.5%
<u>245.1=100.00</u>	

## DICHLORSALICYLATE OF SODIUM.



Obtained by boiling an aqueous solution of the barium salt with sodium carbonate and concentrating the filtered liquid. The salt crystallizes in broad needles, possessing a slight yellow tinge. It is easily soluble in water.

*Sodium Estimation.*

0.1601 Grm. dried salt gave 0.0530 Grm. sodium sulphate=.0171 Grm. sodium=10.68% Na.

Calculated %.	Found %.
$C_6 H_2 Cl_2 OH COO=207=89.95\%$	
+ Na = 23=10.05%	10.68%
<u>229=100.00%</u>	

## DICHLORSALICYLATE OF MAGNESIUM.



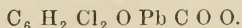
An aqueous solution of the free acid was boiled with magnesium carbonate and the liquid evaporated to a small bulk. After standing some time, small, white crystals appeared; these were very readily dissolved by water.

*Magnesium Estimation.*

.1140 Grm. dried salt gave .0304  $Mg_2 P_2 O_7$ =.0064 Grm. Mg=5.61% Mg.

Calculated %.	Found %.
$(C_6 H_2 Cl_2 OH COO)_2=412=94.50\%$	
+ Mg = 24=5.50%	5.61%
<u>436=100.00</u>	

## DICHLORSALICYLATE OF LEAD.



Lead acetate was added to a solution of the ammonium salt and the lead salt obtained as a white insoluble precipitate, which after being well washed and dried was analyzed.

*Lead Estimation.*

0.1075 grm. dried salt gave .0548 grm. lead = 50.9 % Pb.	
Calculated %.	Found %
$\text{C}_6 \text{H}_2 \text{Cl}_2 \text{O} \cdot \text{C O O} = 205 = 49.76 \%$	
+ Pb = 207 = 50.24 %	50.9 %
$412 = 100.00 \%$	

*Copper Salt.*—Small brown crystals soluble in water.

*Silver Salt.*—White insoluble powder. Decomposed when boiled with water.

## ACTION OF NITRIC ACID UPON DICHLORSALICYLIC ACID.

Dilute nitric acid has no effect upon the acid. When treated with fuming nitric acid no change is produced until heat has been applied. After dissolving the dichlor acid in this solvent I permitted the solution to stand several days, hoping to find the nitro compound separated out by that time—this, however, did not occur. Upon evaporating the solution to dryness, nothing remained, the substance, whatever it may have been, having been completely volatilized. A second portion of the acid after treatment with fuming nitric was mixed with a large quantity of water and then distilled. The distillate possessed a yellow color, and after neutralization with potassium carbonate, was strongly evaporated, then placed in a desiccator over sulphuric acid. After standing some time minute globular crystals appeared, but the quantity being so small I was not able to examine them, preferring to defer the investigation of this nitro compound, if such, until larger quantities of the substance can be obtained.

## CALCIUM OXIDE AND DICHLORSALICYLIC ACID.

The acid distilled with calcium oxide yielded an almost colorless oil, having a rather pungent odor. The compound was not further examined.

## ETHYL DICHLORSALICYLATE.



The introduction of the ethyl radical was first attempted by heating upon a water bath a small flask containing the silver dichlorosalicylate and ethyl iodide. This, however, failed to produce the desired result.

In a second trial the perfectly dry and pulverized silver salt was placed in a tube of Bohemian glass, an excess of ethyl iodide then added, the tube sealed and heated in an air bath for twelve hours, the temperature not exceeding 135°C. Upon examination a rather large quantity of silver iodide was noticed, and the liquid which before heating was colorless was now of a reddish-brown hue. The tube was opened and its liquid contents poured

through a small filter and after washing the silver iodide with alcohol, the filtrate was evaporated upon a water bath. When the liquid had almost approached dryness I observed minute oil globules of a dark color.

The evaporating dish containing these was immediately removed from the water bath and stood in a cool place. In course of a few hours the oil solidified to a dark crystalline mass, which after pressing well between sheets of filter paper, I dissolved in alcohol and after concentration allowed to cool. Beautiful colorless needles separated from the solution. The fusing point was found to be  $47^{\circ}\text{C}$ . Again dissolved and allowed to crystallize the same form of crystals was obtained. The fusing point remained the same.

*Carbon and Hydrogen Estimation.*

0.2072 Grm. well dried substance, burned with lead chromate gave .3418 Grm.  $\text{CO}_2$  45.51 % carbon. And .0808 Grm.  $\text{H}_2\text{O}$  = 4.30 % hydrogen.

Calculated %	Found %
$\text{C}_9 = 108 = 45.96 \%$	45.51 %
$\text{H}_8 = 8 = 3.40 \%$	4.30 %
$\text{Cl}_2 = 78 = 30.21 \%$	
$\text{O}_3 = 48 = 20.42 \%$	

Cahours\* obtained a similar compound by the action of chlorine upon ethyl-salicylate. Broad colorless, shining needles. Fusing point not given. Potassium ethyl-dichlorosalicylate.



This salt was produced by boiling an alcoholic solution of the ether with potassium carbonate. It crystallizes in fine colorless needles, which frequently are united to bundles. Very soluble in alcohol.

The points of difference between the compounds of Cahours, Rogers and myself are in brief these :

The acid of Cahours is but slightly soluble in boiling water. Soluble in boiling alcohol, crystallizing from this in needles and octahedral crystals, and it forms also an insoluble nitro-derivative.

The acid gotten by me is perfectly soluble in boiling water, and in cold alcohol—crystallizing from the former in arborescent masses and from the latter it separates in large colorless needles. The nitro-derivative, if any, is exceedingly soluble.

The acid of Rogers fuses at  $224^{\circ}\text{C}$ , is soluble in boiling water and boiling alcohol. The barium salt has five molecules of water and the copper salt is a green insoluble precipitate.

The acid obtained by me fuses at  $212^{\circ}$ – $214^{\circ}\text{C}$ , its barium salt has but three and half molecules of water and the copper salt forms dark brown warty crystals, soluble in boiling water.

\* *Annalen d. Chemie u. Phar.* 73. 313.